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ATOMIC STRUCTURE STUDIES OF SEMICONDUCTOR-ELECTROLYTE
METAL AND VACUUM INTERFACES(U) STATE UNIV OF NEW YORK
AT ALBANY DEPT OF PHYSICS W M GIBSON ET AL. 12 JAN 82

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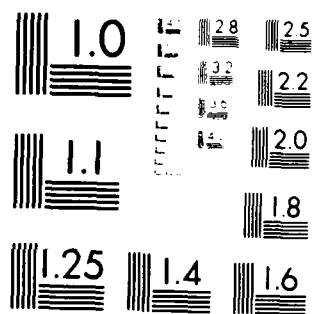
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Department of Physics

State University of New York at Albany

January 12, 1982

TO: Dr. C. T. Lynch, Materials Division
Office of Naval Research
Arlington, VA 22217

FROM: Walter M. Gibson, Department of Physics
State University of New York at Albany
Albany, NY 12222

SUBJECT: End-of-Fiscal-Year Report for ONR Supported Research,
"Atomic Structure Studies of Semiconductor-Electrolyte,
Metal and Vacuum Interfaces"
Contract #: N00014-78C0616 NR 373-039
W.M. Gibson, Principle Investigator
Dr. L.R. Cooper, ONR Scientific Officer

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1. Summary of the Most Significant Technical Results - 1 Oct 81 - 30 Sept 82

The ONR supported surface and interface structure program at the State University of New York at Albany (SUNYA) has two major parts. 1) Ion channeling studies of surfaces and interfaces under Ultra High Vacuum (UHV) controlled conditions and 2) X-Ray Standing Wave Studies under non-UHV conditions.

The ion scattering program has been particularly productive during this period following a three year period of development, training and construction. A large number of publications () and conference presentations () have been made and reprints for a number of these are attached so only the highlights of these studies will be mentioned.

1. Si(100)-Hydrogen Saturated Surface. Extensive reconstruction of the clean 2×1 surface was confirmed and removal of the reconstruction upon adsorption of hydrogen was observed. Absolute hydrogen coverage measurements using a $^3\text{He}(d,p)^4\text{He}$ reaction showed a plateau in the hydrogen uptake at one monolayer corresponding to the monohydride phase with saturation (the dihydride phase) at 1.7 ± 0.1 monolayer. Measurements of the substrate silicon surface structure at saturation hydrogen coverage shows removal of the clean surface reconstruction and enhancement of surface layer vibrational amplitude (by a factor of 2). Off normal direction measurements show that the substrate silicon lattice remains relaxed with the outermost layer displaced inward by $\sim 0.2 \text{ \AA}$ and at least one additional layer also displaced by a significant amount ($> 0.1 \text{ \AA}$).

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2. Epitaxial Interface Studies. We have undertaken a systematic study of structural changes during the early stages of epitaxial film growth. Two systems have been studied, Ge on Si(111) and Ag on Ni(111). Both of these systems show dramatic phase changes at low coverage. At 350°C, germanium grows pseudomorphically (adopting silicon lattice positions), with uniform coverage for the first two monolayers after which the entire germanium overlayer undergoes a phase transition, adopting a characteristic germanium lattice constant in the overlayer. This is the first direct demonstration of Frank Vander Merwe growth in which layer by layer pseudomorphic growth proceeds until sufficient strain is built up because of lattice mismatch to result in a phase transition of the overlayer with generation of misfit dislocations at the interface. Although the lattice mismatch is similar to the Ge/Si(111) case, Ag on Ni(111) behaves strikingly different. The coverage is non-uniform from the beginning. The nickel lattice distorts to adapt to the silver overlayer and a phase transition probably involving a structural change in the silver overlayer which results in removal of subsurface lattice strain occurs at an average coverage of about three monolayers. These examples show the power and versatility of the technique for detailed observation of interface structure changes during epitaxy.

3. Silicon-Metal Silicide Interfaces are Important in Modern Electronic Devices. Studies of silicide growth have failed to show details of bonding or bond breaking during initial silicide formation. A new approach to this problem was undertaken in order to investigate the specific site distribution of the metal during the very first stage (submonolayer) of interaction. This approach involves transmission of an ion beam through a thin (1 μ) silicon crystal which sets up a spatially structured ion flux distribution. The interaction of this channeled beam with adsorbate atoms on the exit surface of the crystal then gives information about the position of the adsorbate relative to the crystal lattice. The initial studies show for the first time that palladium occupies a position along the $\langle 111 \rangle$ axial direction on a Si(111) surface for coverage of less than one monolayer and random position at 6 monolayer coverage. At low coverage it was also found that each palladium atom deposited on the surface displaces more than two silicon atoms from lattice positions by more than 0.5 Å. This apparently large local disorder of the substrate probably accounts for failure of previous LEED and ion scattering results to detect the adsorbate-substrate registration. Gold on a Si(100) surface exhibits complex behavior. At submonolayer coverage the gold is registered along (110) planes perpendicular to the surface but does not have fixed position relative to the surface normal $\langle 100 \rangle$ axis. At such coverage the gold does not disorder the substrate - on the contrary, the clean surface reconstruction is removed even for gold coverage of ~ 0.5 monolayer. From one to about four monolayer coverage the gold adsorption site becomes fixed along 100 rows and above 4 monolayers becomes random.

4. A systematic study of the technologically important Si-SiO₂ interface has shown this interface to be very abrupt with less than two monolayers of silicon displaced from ideal lattice positions and that less than one monolayer of SiO is present before establishment of a stoichiometric SiO₂ random structure. The silicon displaced at the interface is mostly moved from ideal lattice position in a direction normal to the surface and then only by a small amount (~ 0.1 Å).

5. X-Ray Standing Wave Interface Spectroscopic (XSWIS) studies have been carried out of bromine adsorbed on Si(111) and Si(110) surfaces from methanol solution. It was demonstrated that both lateral and normal position determinations

could be made with precision of 0.02 \AA for coverage as small as 0.1 monolayer. Such measurements have been made in-situ, i.e. in the presence of a thin liquid layer and in gaseous ambient conditions. Measurements by bromine adsorbed on Si(100) surfaces in air show remarkable stability with desorption rates dependent on relative humidity. At 100% humidity the desorption time (for desorption of $\frac{1}{2}$ the bromine correlated with the lattice) is several hours and for 0% humidity is at least several days. On Si(111) surfaces the desorption is even slower. One conclusion of the study is that substrate relaxation and reconstruction is removed by bromine adsorption. This is clearly a very powerful technique for microscopic studies of interfaces such as the solid-liquid interface that have not been accessible before.

II. Technological Significance

The demonstrated ability to investigate the microscopic structural behavior of surfaces and especially buried interfaces has widespread significance since such interfaces affect and often control the properties of modern and proposed microelectronic devices. Our work is concentrated on semiconductor-metal, semiconductor-oxide and semiconductor-electrolyte interfaces. Already, for example, the results of our study of the Si-SiO₂ interface is causing a basic change in the ways that one approaches the important question of electronic states at this interface. The increasing importance of multilayer structures and even superlattice structures in electronic and optical systems makes the science of epitaxial crystal growth very important. The almost unique ability of high energy ion channeling and X-Ray Standing Wave techniques to study epitaxial growth at buried interfaces has caused us to emphasize this type of study. Finally, the prospect to obtain microscopic structural information about processes occurring at the solid-liquid interface is exciting because of its relevance to a wide variety of corrosion, catalytic, plating and other processes.

III. Presentations, ONR Reports and Publications - 1 Oct 81 to 30 Sept 82

Presentations

28th National Symposium of the American Vacuum Society, Anaheim, CA, November 1981

X-Ray Standing Wave Analysis for Bromine Chemisorbed on Si
M.M. Bedzyk, W.M. Gibson and J.A. Golovchenko

Transmission Channeling Studies of Metal Interaction with Silicon
R. Haight, T. Itoh, T. Narusawa, W.M. Gibson and A. Hiraki

Epitaxial Growth of Germanium on Si(111) Studied by High Energy Ion Channeling
T. Narusawa and W.M. Gibson

Materials Research Society, Boston, MA, November 1981

Initial Structural Study of the Stages of Metal-Silicide Formation (Invited Paper)
A. Hiraki, T. Narusawa and W.M. Gibson

American Physical Society, Dallas, TX, March 1982

Structure Study of Epitaxial Interface Formation by High Energy Ion Scattering

W.M. Gibson, R. Haight, T. Itoh and T. Narusawa

X-Ray Standing Wave Analysis for the Photoadsorption of Bromine on Silicon

M.J. Bedzyk, W.M. Gibson, G.D. Gillispie and J.A. Golovchenko

Atomic Structure of H-Saturated Si(100) Surface Studied by High Energy Ion Scattering

W.M. Gibson, T. Narusawa, K. Kinoshita and L.C. Feldman

International Workshop on Ion Beam Studies of Surface and Interface Structure, July 1982

Informal, two day workshop in which all aspects of ion channeling studies of surface and interface structure were discussed. Sponsored by SUNY-Albany. Co-chaired by W.M. Gibson, SUNYA and L.C. Feldman, Bell Laboratories. Attended by representatives of all active and some prospective groups involved with such studies.

Attendees: J.U. Andersen, Aarhus; J. Barrett, ORNL; W.K. Chu, N. Carolina, N. Cheung, Berekley; C. Cohen, Paris; R. Culbertson, ORNL; J. Davies, Chalk River; V. Dose, Wurzburg; L.C. Feldman, Bell Labs; T. Gustofson, U. of Penn; J. Gyulai, Cornell; Y. Kuk, Bell; P. Norton, Chalk River; C. Palmstrom, U. of Penn; H. Roosendahl, Gronigen; S. Samanta, U. of Maine; R. Smith, U. of Montana; E. Tornquist, U. of Penn; W. Unertl, U. of Maine.

Gordon Conference on Particle-Solid Interactions, Plymouth, NH, July 1982

Ion Beam Studies of Si-SiO₂ Interface (Invited paper)

R. Haight, L.C. Feldman and W.M. Gibson

Ion Beam Studies of the Early Stages of Epitaxy (Invited paper)

W.M. Gibson

Second International Symposium on Molecular Beam Epitaxy and Related Clean Surface Techniques, Tokyo, August 1982

Ion Beam Studies of the Initial Stages of Epitaxial Film Growth (Invited)

W.M. Gibson

During this period invited colloquium and seminar talks were given at:

University of Maine, Orono
University of Maryland, College Park
University of Utah, Salt Lake City
University of Tokyo
Osaka University
Nagoya University
Fudan University, Shanghai
Nanking University
Institute of Nuclear Physics, Shanghai
University of Sichuan, Chendong
Xian Jiaotong University, Xian

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Publications

Transmission Channeling Studies of the Pd/Si(111) >x7 System

R. Haight, T. Itoh, T. Narusawa and W.M. Gibson

J. Vac. Sci. Technol. 20, 689 (1982)

Interface Structure of Epitaxial Ge-Si(111) System Studied by High Energy Ion Scattering

T. Narusawa and W.M. Gibson

J. Vac. Sci. Technol. 20, 709 (1982)

X-Ray Standing Wave Analysis for Bromine Chemisorbed on Silicon

M.J. Bedzyk, W.M. Gibson, and J.A. Golovchenko

J. Vac. Sci. and Technol. 20, 634 (1982)

Atomic Structure at the (111) Si-SiO₂ Interface

R. Haight and L.C. Feldman

J. Appl. Phys. 53, 4884 (1982)

X-Ray Standing Wave Analysis for Bromine Chemisorbed on Silicon (Thesis)

M.M. Bedzyk

IV. Other Research of Principle Investigator

A. Synchrotron Based Studies of Semiconductor Surfaces and Interfaces.

In a joint project together with Dr. Jene Golovchenko of Bell Laboratories and Professor B. Batterman of Cornell University, the X-Ray Standing Wave Interferometry Studies of Surfaces and Interfaces are being extended to the use of Synchrotron Radiation sources. This is an extension of the XSWIS studies described above and are complementary to the x-ray tube based studies which will continue to be the testing ground for new systems and will be the major tool for integrating this technique with in-situ electrochemical studies. The Synchrotron based work is supported by the National Science Foundation with a current annual budget of \$75,000.

B. High Energy Channeling Studies. As a participant in a program to study applications of particle channeling at very high energies, W. Gibson serves principally in an advisory capacity. The principle investigator and supervisor of this program is Professor C.R. Sun of SUNY-Albany. The experimental studies are carried out at Fermi National Accelerator Lab and Stanford Linear Accelerator Laboratory. This program is supported by the U.S. Department of Energy with a current annual budget of \$185,000.

V. Participants

W. Gibson, Professor of Physics, SUNY-Albany, Program Director

Dr. Tadashi Narusawa, Post-doctoral Research Associate, until Feb. 1982

Dr. Toshimichi Itoh, Post-doctoral Research Associate

Mr. Michael Bedzyk, Graduate Student, graduated July 1982

Mr. Bupendra Dev, Graduate Student

Mr. Richard Haight, Graduate Student

Mr. Hans Gossmann, Graduate Student

Mr. Han Sheng Jin, Graduate Student

Research Collaborators (unsupported)

Dr. Jene Golovchenko, Bell Laboratories

Dr. Leonard C. Feldman, Bell Laboratories

Dr. Volker Dose, Visitor from Wurzburg University

ACKNOWLEDGMENTS

I would like to take this opportunity to thank my family, friends and teachers for their help and support.

I consider myself very fortunate in having been associated with Dr. Walter M. Gibson and Dr. Jene A. Golovchenko. Their experience and knowledge have proven to be a valuable source of information.

I am grateful for the assistance given by: P. Cowan of NBS, N. Hertel, B. Krawchuk, B. Dev, K. Horn, R. Hendrix, A. Haberl, C. Pauley, G. Gillespie, R. Stamp, P. Ge, R. Kleinhenz, C. Mitra and K. Webster of SUNYA, and J. Patel and P. Freeland of Bell Labs.

The financial support for this research was provided by the Office of Naval Research, under contract No. 00014-78-C-0616.

This thesis is dedicated to my wife Franziska.

W. Gibson

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X-Ray Standing Wave Analysis for
Bromine Chemisorbed on Silicon

by

Michael J. Bedzyk

A Dissertation

Submitted to the State University of New York at Albany

in Partial Fulfillment of

the Requirements for the Degree of

Doctor of Philosophy

College of Arts and Sciences

Department of Physics

1982

PACS Index No.

68.20.+t

Abstract Submitted
for the Dallas Meeting of the
American Physical Society

Mar. 6-12, 1982

Date

Suggested title of
session in which paper
should be placed
Surface Structure

X-ray Standing Wave Analysis for the Photo-adsorption of Bromine on Silicon* M.J. Bedzyk, W.M. Gibson, G.D. Gillispie, SUNY-Albany, and J.A. Golovchenko, Bell Laboratories.--The X-ray standing wave method¹ has proven to be a uniquely sensitive structural probe for determining the surface interfacial position of chemisorbed impurity atoms², which are commensurate with the Bragg diffraction planes of the adsorbent single crystal. Besides yielding adsorbate positional information (with an accuracy of 0.04 Å), the technique is also useful for measuring the commensurate and incommensurate fractional coverages of the adsorbate impurity atom. In situ measurements (using methanol as a solvent) and open air measurements have been performed on the Br/Si(220) and the Br/Si(111) surface interfaces. In these measurements the photochemistry used for producing such interfaces was studied by observing the relative efficiency of commensurate Br chemisorption at various u.v. and visible light wavelengths.

* Supported by the Office of Naval Research under Contract No. N00014-78-C-0616.

1) S.K. Anderson, J.A. Golovchenko, G. Mair, Phys. Rev. Lett. 37, 1141 (1976).

2) P.L. Cowan, J.A. Golovchenko, M.F. Robbins, Phys. Rev. Lett. 44, 1680 (1980).

- () Prefer Poster Session
(x) Prefer Standard Session
() No Preference

Wilfried W Scholz

Signature of APS Member

Wilfried W. Scholz

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